

L Number	Hits	Search Text	DB	Time stamp
-	421	karrer.in.	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/31 08:09
-	56	karrer.in. and silicone	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/24 15:32
-	0	(karrer.in. and silicone) and mignana	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/24 15:32
-	15	(karrer.in. and silicone) and mignani	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/24 15:32
-	27210	hindered adj amine adj light adj stabilizer or hals	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:13
-	313111	silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/31 08:10
-	2606	(hindered adj amine adj light adj stabilizer or hals) and (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/24 15:57
-	914	organohydrogen adj siloxane or organohydrogensiloxane	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/24 15:57
-	1782	vinyl adj siloxane or vinylsiloxane	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/29 16:07
-	1	((hindered adj amine adj light adj stabilizer or hals) and (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)) and (organohydrogen adj siloxane or organohydrogensiloxane) and (vinyl adj siloxane or vinylsiloxane)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/24 15:58
-	313111	silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/08 07:55
-	914	organohydrogen adj siloxane or organohydrogensiloxane	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/29 16:07
-	1782	vinyl adj siloxane or vinylsiloxane	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/28 08:23

-	140	(organohydrogen adj siloxane or organohydrogensiloxane) and (vinyl adj siloxane or vinylsiloxane)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/28 08:23
-	27210	hindered adj amine adj light adj stabilizer or hals	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/08 07:55
-	1	((organohydrogen adj siloxane or organohydrogensiloxane) and (vinyl adj siloxane or vinylsiloxane)) and (hindered adj amine adj light adj stabilizer or hals)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/28 08:27
-	2606	(silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone) and (hindered adj amine adj light adj stabilizer or hals)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/28 08:27
-	1	((silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone) and (hindered adj amine adj light adj stabilizer or hals)) and ((organohydrogen adj siloxane or organohydrogensiloxane) and (vinyl adj siloxane or vinylsiloxane))	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/28 08:28
-	27234	hindered adj amine adj light adj stabilizer or hals	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/29 15:30
-	313338	silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/29 15:30
-	17793	(unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/30 08:21
-	234	(hindered adj amine adj light adj stabilizer or hals) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone))	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/29 15:57
-	0	alternating adj cyclic adj hydrocarbon adj residue	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/29 15:57
-	1784	vinyl adj siloxane or vinylsiloxane	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/29 16:07
-	914	organohydrogen adj siloxane or organohydrogensiloxane	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/29 16:07

-	0	((hindered adj amine adj light adj stabilizer or hals) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone))) and (vinyl adj siloxane or vinylsiloxane) and (organohydrogen adj siloxane or organohydrogensiloxane)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/29 16:08
-	0	((hindered adj amine adj light adj stabilizer or hals) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone))) and (organohydrogen adj siloxane or organohydrogensiloxane)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/29 16:08
-	0	((hindered adj amine adj light adj stabilizer or hals) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone))) and (organohydrogen adj siloxane or organohydrogensiloxane)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/29 16:08
-	313338	silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/30 08:19
-	27234	hindered adj amine adj light adj stabilizer or hals	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/30 08:19
-	10655	(hydrogen or H or hydride) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/30 08:20
-	11134	(hydrogen or H or hydride or organohydrogen or organohydrogensiloxane) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/30 08:21
-	17793	(unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/30 08:23
-	3893	((hydrogen or H or hydride or organohydrogen or organohydrogensiloxane) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone))	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/30 08:23

-	16	(hindered adj amine adj light adj stabilizer or hals) and (((hydrogen or H or hydride or organohydrogen or organohydrogensiloxane) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)))	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/30 08:24
-	8	((hindered adj amine adj light adj stabilizer or hals) and (((hydrogen or H or hydride or organohydrogen or organohydrogensiloxane) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)))) and filler	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/30 09:06
-	0	((hindered adj amine adj light adj stabilizer or hals) and (((hydrogen or H or hydride or organohydrogen or organohydrogensiloxane) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)))) and filler) and light adj bulb	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/30 08:25
-	12667	"16" and light adj bulb	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/30 08:25
-	0	((hindered adj amine adj light adj stabilizer or hals) and (((hydrogen or H or hydride or organohydrogen or organohydrogensiloxane) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)))) and light adj bulb	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/30 08:25

-	8	((hindered adj amine adj light adj stabilizer or hals) and ((hydrogen or H or hydride or organohydrogen or organohydrogensiloxane) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)))) or ((hindered adj amine adj light adj stabilizer or hals) and ((hydrogen or H or hydride or organohydrogen or organohydrogensiloxane) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)))) and filler)) not ((hindered adj amine adj light adj stabilizer or hals) and ((hydrogen or H or hydride or organohydrogen or organohydrogensiloxane) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)))) and filler)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/30 10:52
-	83103	general adj electric	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/30 10:52
-	313338	silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:13
-	12045	(general adj electric) and (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/30 10:53
-	27234	hindered adj amine adj light adj stabilizer or hals	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/30 10:53
-	155	((general adj electric) and (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)) and (hindered adj amine adj light adj stabilizer or hals)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/30 10:54

-	1854	(524/86 252/582 252/588 252/589).ccls.	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/31 08:09
-	313722	silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/31 08:10
-	27246	hindered adj amine adj light adj stabilizer or hals	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/31 08:10
-	6	((524/86 252/582 252/588 252/589).ccls.) and (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone) and (hindered adj amine adj light adj stabilizer or hals)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/31 08:16
-	39	"4421823"	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/31 08:17
-	1	"4421823" and polysiloxane	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/31 08:16
-	1	"04421823"	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/31 08:17
-	1	de-4421823-\$.did.	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/10/31 08:18
-	328166	silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:17
-	28130	hindered adj amine adj light adj stabilizer or hals	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:13
-	0	alternating adj cyclic adj hydrocarbon adj residue	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:25
-	2826	(silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone) and (hindered adj amine adj light adj stabilizer or hals)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:16
-	73480	polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:18

-	66	(polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane) same (hindered adj amine adj light adj stabilizer or hals)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:18
-	282	(silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone) same (hindered adj amine adj light adj stabilizer or hals)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:18
-	293	(polycyclic or cyclic) adj hydrocarbon adj residue	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:25
-	2838	((silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone) and (hindered adj amine adj light adj stabilizer or hals)) not8	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:26
-	2823	((silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone) and (hindered adj amine adj light adj stabilizer or hals)) not ((polycyclic or cyclic) adj hydrocarbon adj residue)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:26
-	3	((silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone) and (hindered adj amine adj light adj stabilizer or hals)) and ((polycyclic or cyclic) adj hydrocarbon adj residue)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:27
-	11	((silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone) and (hindered adj amine adj light adj stabilizer or hals)) not ((polycyclic or cyclic) adj hydrocarbon adj residue)) and light adj bulb	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:28
-	66	(polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane) same (hindered adj amine adj light adj stabilizer or hals)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:29
-	0	((polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane) same (hindered adj amine adj light adj stabilizer or hals)) and light adj bulb	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:28
-	854	(polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane) and (hindered adj amine adj light adj stabilizer or hals)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:29
-	3	((polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane) and (hindered adj amine adj light adj stabilizer or hals)) and light adj bulb	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:36
-	1	(non-cyclic or noncyclic) near5 vinylsiloxane	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:37

-	1	(non-cyclic or noncyclic) near10 vinylsiloxane	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:39
-	1129	vinylsiloxane	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:39
-	957	(organohydrogen adj siloxane or organohydrogensiloxane)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:39
-	354862	filler	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:40
-	82	vinylsiloxane and ((organohydrogen adj siloxane or organohydrogensiloxane)) and filler	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:43
-	1	(vinylsiloxane and ((organohydrogen adj siloxane or organohydrogensiloxane)) and filler) and (hindered adj amine adj light adj stabilizer or hals)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:41
-	1058	(silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone) and vinylsiloxane	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:41
-	108	((silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone) and vinylsiloxane) and ((organohydrogen adj siloxane or organohydrogensiloxane))	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:41
-	1	((silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone) and vinylsiloxane) and ((organohydrogen adj siloxane or organohydrogensiloxane))) and (hindered adj amine adj light adj stabilizer or hals)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:41
-	109	vinylsiloxane and ((organohydrogen adj siloxane or organohydrogensiloxane))	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:46
-	10	vinylsiloxane adj fluid	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:46
-	2826	((silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone) and (hindered adj amine adj light adj stabilizer or hals)) not8) and (hindered adj amine adj light adj stabilizer or hals)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:46

-	0	(vinylsiloxane adj fluid) and (hindered adj amine adj light adj stabilizer or hals)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:53
-	0	sle5700	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:53
-	3	sle adj "5700"	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 10:54
-	0	(sle adj "5700") and (hindered adj amine adj light adj stabilizer or hals)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 11:00
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-	272	((vinyl or allyl or olefin\$2 or unsaturat\$3) near10 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)) and (hindered adj amine adj light adj stabilizer or hals)) and filler	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 11:22
-	216	((vinyl or allyl or olefin\$2 or unsaturat\$3) near10 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)) and (hindered adj amine adj light adj stabilizer or hals)) and filler) and crosslink\$3	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/07 11:23
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-	254	divinyl near3 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/08 07:57
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-	96	((vinylsiloxane or divinylsiloxane) and organohydrogensiloxane) and filler	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/08 10:27

-	8	((vinylsiloxane or divinylsiloxane) and organohydrogensiloxane) and filler) and divinyl	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/08 09:09
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-	46	uvasil near2 "299"	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/08 11:00

-	15	(uvasil near2 "299") and (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone)	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/08 11:03
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-	4	3775452.pn.	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/08 13:06



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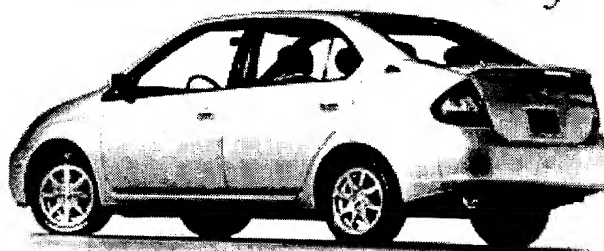
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Posted on: 10/01/2001

UV Protection and Coatings for Plastics in the Automobile Industry

UV Protection and Coatings for Plastics

in the Automobile Industry



Since Henry Ford launched his famous Model T, the development of automobile engineering has experienced true quantum leaps. Because of the variety of possible safety considerations and the significant weight savings, the automotive industry is using plastic components. On average, today's car consists of 14% of various types of plastic. The organic material is, however, subject to a natural aging process that makes the use of stabilizers necessary. Exposure to sunlight accelerates the process. Often, such plastic components are treated with a topcoat. However, due to undesired migration, the amount of stabilizer in the plastic and coating decreases over time. The plastic, as well as the coating, is then no longer sufficiently protected. This article describes the mechanism of migration and explains possible methods of delaying it.

Plastics

Plastics are found in the car as cable insulation, interior covering, dashboards, tanks or under the hood. Increasingly, auto body components are also being made of plastic. Some of these are uncoated or appear in the same shade as the rest of the auto body. Some pilot projects even describe auto bodies made entirely of plastic.

The material itself is subject to a natural aging process, which begins as early as

manufacture, due to extreme processing conditions that occur at times. To delay the degradation as long as possible, so-called process and long-term stabilizers are added. If the component is exposed to the elements without protection, degradation is further accelerated. In addition to the compulsory long-term stabilization, the polymer also needs an additional UV-stabilization package.

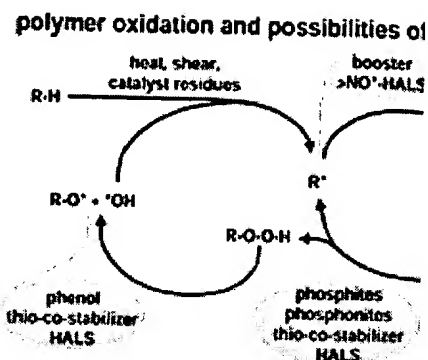


Figure 1

Coatings

The UV stabilization is an indispensable element of the plastic coating in the automobile exterior. In ideal circumstances, these are multi-layer systems. The coating of plastics begins with the application of a primer, which has a binding effect on the basecoat, that is then applied over the primer. Finally, a clearcoat containing the light stabilizers for UV protection seals the coating system.

act as oxygen radical traps

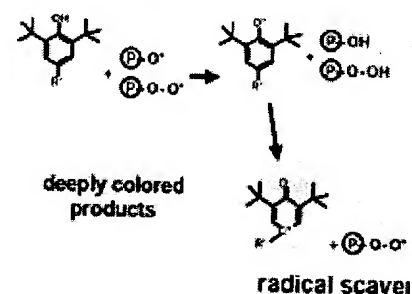


Figure 2

This, however, exacerbates the problem of migration¹: the organic substrate makes it possible for the stabilizers to migrate into the plastic and also permits the migration of the plastic stabilizers to the coating. With a decrease in the concentration of UV protector in the paint's protective function of the coating, by definition, also decreases. Plastic stabilizers upwards from the substrate cause yellowing in the topcoat or, in the worst case, to complete loss of adhesion.

Polymer Stabilizer Packages

Every stabilizer has a specific temperature range in which it develops its optimum protective effect. For this reason, a mix of different stabilizers is added to the polymers - so-called stabilizer packages. They generally consist of primary and secondary antioxidants, and ensure sufficient protection of the polymer (see Figure 1).

The most important primary antioxidants are the sterically hindered phenols. They are suitable as long-term stabilizers in almost all cases. Despite their many benefits, they have one undesirable side effect. As a result of UV radiation and subsequent photolytic degradation, they develop deeply colored quinoid structures which lead to a yellowing of the plastic (see Figure 3).

how do UV-absorbers work ?

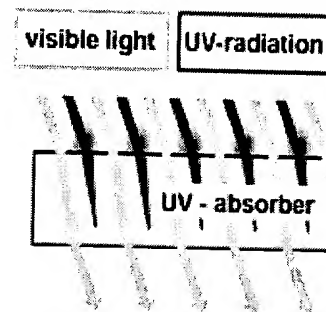


Figure 3

As protection against the often high temperatures during further processing, secondary antioxidants such as phosphites, phosphonites or HALS are also used.

Coating Stabilizer Packages

Two groups of stabilizers have been developed for coatings and are suitable for plastics and the coatings themselves: UV absorbers and sterically hindered amine (HALS = Hindered Amine Light Stabilizers).³

UV Absorbers

Most UV absorbers function according to similar mechanisms. The physical absorption process protects both the deeper sections of the coating and the substrate from the high-energy fractions of sunlight. These are absorbed and lead to isomerization, causing the molecule to transform into an excited structure. When the molecule reverts to its original condition, the absorber releases the energy into the environment as thermal energy. The relevant UV absorbers in coatings include 2-hydroxybenzophenones, oxalanilides, 2-hydroxyphenylbenzotriazoles and 2-hydroxy-phenyltriazines.

how does HALS work ?

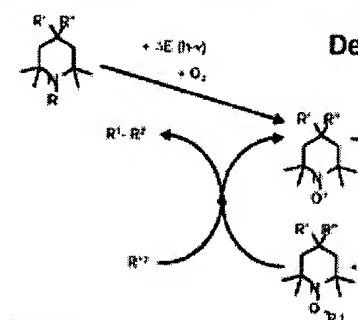


Figure 4

According to the Lambert-Beer Law, the absorption of a medium depends, among on the UV-absorber concentration and on the distance traveled within it by the light concentration and the thickness of the coating may, therefore, not be permitted to certain minimum limit in order to guarantee protection of the substrate through absorption. Deeper the UV ray penetrates the coating, the greater the absorption or the effect absorber. Due to the very short distance the UV ray is able to travel to the immediate coating, the protective effect of the UV absorber is at its lowest at this point (s

Sterically Hindered Amines (HALS)

With UV protectors of the hindered amine light stabilizer type, stabilization results from the trapping of the intermediately developed radicals. All UV protectors of this type are based on a single chemical structure: tetramethyl-piperidine. They differ only in terms of the substituents at the nitrogen atom (R) or on the opposite ring side (R' and R'').

They operate as UV protectors by combining with oxygen when exposed to light to form stable nitroxide radicals. The latter trap the radicals, which have developed from the polymer through exposure to UV rays. The most important feature of the nitroxide radicals is their capacity. Thus, a cyclical reaction is possible, which can repeat hundreds of times. HALS itself has been degraded (see Figure 4). Radical chain reactions, which attack the substrate, are thus prevented.

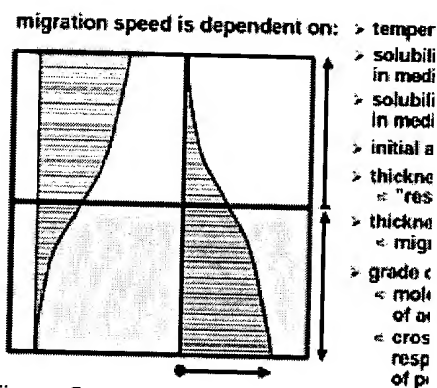


Figure 5

HALS, in contrast to UV absorbers, protect chemically rather than physically. Their effectiveness depends on optimum dispersal in the binding agent. The necessity of HALS is therefore based on the solids content in the binding agent.

Migration Processes

Migration is the undesired movement of the stabilizers between the coating layers and the substrate. Whether migration proceeds from the upper layer to the substrate or vice-versa -- negative effects

occur in both cases. Among other things, the stabilizing properties of the coating may be lost or a degradation of the plastic may occur. The speed of migration depends on a variety of factors, including the temperature, solubility of the additives, concentration differences, the thickness of the coating or the mobility of the additive.²

While migration cannot be completely prevented, it can be effectively delayed and controlled by the following.

- Harmonization of plastics and coating stabilizers
- Use of "non-migrating" stabilizers
- Migration barriers

In principle, migration can also be reduced through the use of high molecular – ar consequently lower mobile – additives. The parameters of the molecular weight c however, be varied at will, as it has a simultaneous effect on the secondary prope solubility and compatibility.

Detection through Microtome Technology

The microtome technique is a modern method of tracing migration. Working from the outside, it separates coatings into thin layers thus permitting a detailed analysis of the protective layers. Depending on the hardness and brittleness of the material to be examined, suitable setting of the microtome permits sections of as little as 2 mm to be cut. In order to obtain intact and usable sections, the plastic samples are generally somewhat thicker. Subsequently the sections, which can be up to 7 x 9 cm, are placed in test tubes, mixed with an extraction agent and left in an ultrasonic bath for 10 hours. Afterwards, the concentration of the additive in each individual layer can be determined by HPLC or gas-chromatographic means (HALS and UV-absorber).

mechanism of photo-reactive t

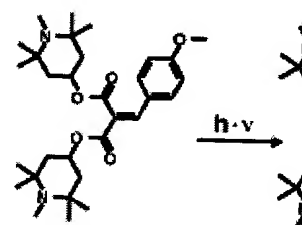


Figure 7

Methods of Reducing Migration

Harmonization of Plastics and Coating Stabilizer

HALS stabilize both the plastic and the coating. In the protective coating, the HAL together with a suitable UV absorber as light stabilizers. In plastics, on the other h often needed for process stabilization.

Whereas it was common up to now for each manufacturer to use the stabilizer of latest studies from Clariant prove the benefit of using identical stabilizers in the pr coating and the plastic. Otherwise the additive concentration in the protective laye significantly due to the extremely high level of migration, causing stabilization to b ineffective. The adhesive properties of the coating decrease, the component is su discoloration and loss of gloss.

The contrasting results achieved through the use of the same HALS in plastic and layer – the clearcoat – are shown in Figure 6. Here, too, a migration process occi specified experimental conditions. However, the concentration profile confirms a s slower migration process. The use of the same additive therefore leads to a reduc

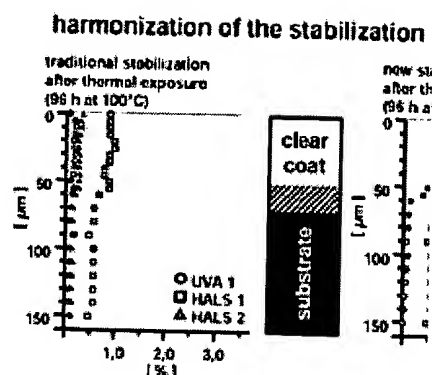


Figure 6

This new process, however, demands close cooperation between the manufacturer and the suppliers of plastics. This is because the same stabilizers can only be used with consultation. Apart from the increased stability, the laborious process of manufacturing layer systems can be avoided, considerably reducing production costs. However, this process cannot be universally applied. Further points also remain troubling such as the complex logistic requirements due to the wide spectrum of colors or the realization of meta-

Various possibilities exist for directly preventing the migration of HALS. Oligomer example, are so large that they adhere to the surrounding polymer matrix and migrate. A further variant is graftable HALS. These are chemically linked directly to the binder and are therefore not capable of any migration. Very special perspectives are offered by photo-reactive HALS Sanduvor PR-31.

Migration Barriers

A higher crosslink density of the polymer matrix may contribute to the reduction of migration speed as well. With increased crosslink density, the gaps in the polymer become smaller, holding back larger additives. This variant is, however, of only little relevance, as excessive crosslink density leads to embrittlement of the coating.

Plastic components are having a determining influence on modern automobile construction. Plastic will be a decisive factor in shaping the car of the future due to their manifold advantages. As a result, the development of efficient and cost-cutting coating systems for this special material is becoming increasingly important. The most significant finding is that plastic and paint components beneficially contain identical stabilizers. The migration process is considered as a result and the expensive application of a multi-layer system becomes unnecessary. However, close cooperation between plastics supplier and coating manufacturer is highly appreciated.

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Symposium, June 4-6, 2001, in Troy, MI.

For more information on coatings for plastics, contact Gerd Faoro, Pigments and Division, Polymer Additives BL, Boite Postale 149, 68331 Huningue, Cedex, France

*phone 0033-389-89-6172; fax 0033-389-89-6195; e-mail Gerd.Faoro@clariant.com
Number 132.*

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